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Poly(ethylene-co-methacrylic acid)-Zinc 이오노머의 수소결합에 관한 연구

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Hydrogen Bonding in Poly(ethylene-co-methacrylic acid)-Zinc Ionomer

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요 약 : 부분적으로 중성화된 에틸렌-메타크릴산 공중합체(EMAA)-Zn 이오노머의 수소결합 형성에 대한 온도 의존성을 적외선 분광분석으로 조사하였다. EMAA-Zn 이오노머의 이온화되지 않은 상태로 남아있는 카르복실산들은 acid dimer를 형성하거나 carboxylic acid salt 형태의 수소결합을 한다. 카르복실산 C=O 흡수 피크의 면적으로부터 이들 수소결합생성에 관한 열역학적 파라미터를 계산하였다. 부분적으로 중성화된 EMAA-Zn 이오노머에서의 acid dimer 생성 엔탈피는 −4.55 kcal/mol이었으며, carboxylic acid salt 생성 엔탈피는 −8.87 kcal/mol이었다. 부분적으로 중성화된 EMAA-Zn 이오노머에서의 acid monomer-dimer의 평형은 carboxylic acid salt 형성에 의해서 영향받는다는 것을 알 수 있었다.

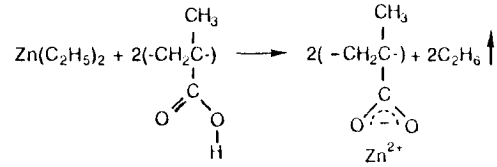
Abstract : Temperature dependences of hydrogen-bond formation in a partially neutralized poly(ethylene-co-methacrylic acid)(EMAA)-Zn ionomer have been investigated by infrared spectroscopy. Unionized carboxylic acid groups remaining in a partially neutralized EMAA-Zn ionomer form two types of hydrogen bonds : carboxylic acid dimers and carboxylic acid salts. Thermodynamic parameters for these hydrogen bond formations were calculated by using integrated absorbances of the carboxylic acid carbonyl peaks. Enthalpies of −4.55 and −8.87 kcal/mol for the acid dimerization and carboxylic acid salt formation in a partially neutralized EMAA-Zn ionomer, respectively, were obtained. It is shown that the carboxylic acid monomer-dimer equilibrium in the partially neutralized EMAA-Zn ionomers is affected by the carboxylic acid salt formation between carboxylic acid and carboxylate groups.

INTRODUCTION

Ionomers are ion-containing polymers with hydrocarbon backbones that contain a relatively small amount of functional groups(e. g. carboxylic, sulfonic, or phosphoric acids, etc.) which are partially or completely neutralized, either present as pendant groups or directly incorporated into the main chain. Research on the microstructure of ionomers has been extensive over the past two decades because of the unique physical properties that these materials possess. The presence of ionic groups in the polymer changes some of its physical properties dramatically, for example, the increase in modulus, viscosity, and glass transition temperature, etc. The unique physical properties of ionomers appears to be due in some way to aggregation of the ionic species in these systems. Most of the research done on these materials has been devoted to the determination of the structure and size of the ionic domains and the correlations between molecular structure and the resulting properties, which are still matters of considerable uncertainty. Detailed discussions of these issues are given in a number of excellent books and reviews.[1~7]

Several models of the microstructure of ionomers have been proposed, some based primarily on the interpretation of mechanical and spectroscopic data and some based on the analysis of small-angle X-ray scattering data. However, the most commonly accepted model is the multiplet-cluster model proposed by Eisenberg.[8] Multiplets are localized structures describing the arrangement of ionized acid groups around specific cations. Clusters, on the other hand, are defined as groups of several multiplets that form a domain in the material which is locally rich in ionic species but also contains a significant amount of hydrocarbon as well. Many spectroscopic experiments including dielectric, infrared, and Raman spectroscopies have indicated that there are two different ion environments, and these have usually been interpreted as corresponding to multiplets and clusters.

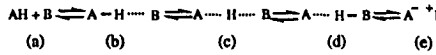
Several years ago, Coleman et al. have reported the results of a series of infrared studies of ethylene-co-methacrylic acid(EMAA) copolymer films that had been completely neutralized with various metal cations.[9~12] Emphasis was placed upon the interpretation of the fine structure present in the carboxylate asymmetric stretching region of the infrared spectra of various metallic salts of an EMAA copolymer. These bands coalesce into a single broad entity upon annealing at room temperature for extended periods of time.[9,10] They have previously rationalized such observations in terms of the model of multiplet-cluster formation proposed by Eisenberg.[8] More recently, they have reported the revaluation of this interpretation as a result of the effect of water absorption on the carboxylate stretching modes of various ionomers.[12] This observation necessitated to reexamine a specific metallic ionomer which could be prepared under a strictly anhydrous condition. Consideration of the byproducts of neutralization reaction led one to have the choice of diethylzinc($ZnEt_2$) as an appropriate metallic compound to prepare fully and partially neutralized EMAA-Zn ionomer films. The reaction of the acid groups with $ZnEt_2$ results in the evolution of ethane gas which escapes and thus does not complicate the spectrum of the neutralized product.



In a recent paper,[13] the carboxylic acid salt structure has been imported to interpret the temperature dependent infrared spectral results of the partially neutralized EMAA-Zn ionomers prepared using $ZnEt_2$. The carboxylic acid salts, which are compounds involving strong hydrogen bonds between carboxylic acid and carboxylate groups, have been largely ignored in previous studies of the microstructure of ionomers.

There is a wealth of literature concerning the

nature of hydrogen bonds in all their manifestations, summarized in various major reviews and books.[14~18] One of the useful classifications of the hydrogen bonds that ultimately depends upon the A···B interatomic distance is based on the different potential energy curves corresponding to the various species depicted in the following equilibrium scheme :



where AH and B represent the proton donor and acceptor for the hydrogen bond formation, respectively.

For weak or moderately strong hydrogen bonds the hydrogen atom is located closer to one atom or the other(depicted as (b) and (d) above). One aspect of these fundamentals which is relevant to the present study is the special case of acid salt with very short hydrogen bonds found in small molecules reviewed by Speakman.[19] As the strength of the hydrogen bond increase and the A···B length decreases, the hydrogen atom is not so clearly identified as more strongly associated with one atom or the other(depicted as (c) above). Such an interpretation of the formation of very short hydrogen bonds in the zinc salt of EMAA copolymer may be echoed in Mauritz's report[20] on the proton tunneling within the hydrated perfluorosulfonate ionomer membrane.

In this paper are reported the results of an infrared spectroscopic study on the film of an EMAA copolymer partially neutralized with zinc cation. The degree of neutralization of the EMAA copolymer was determined by analysis of the infrared spectra. The equilibrium constants and enthalpies of hydrogen bond formation for carboxylic acid dimerization and zinc acid salts formation of the partially neutralized zinc ionomer were obtained from temperature-dependent infrared studies.

EXPERIMENTAL

The ethylene-methacrylic acid(EMAA) copolymer used in this study was obtained from the laboratory of the E. I. du Pont de Nemours & Co. The EMAA copolymer used in this study was reported to contain 26 weight % methacrylic acid (MAA) and is denoted EMAA[26]. On the molar basis, this corresponds to 10.3 mole % MAA. Assuming a random distribution of MAA units in the copolymer, this yields an average number of 19 methylene units per MAA unit. Results obtained from differential scanning calorimetry(DSC) indicate that the EMAA[26] copolymer crystallize to a very limited extent ; presumably polyethylene-type crystallinity is formed from the large sequences of methylene units. Multiple peaks were observed in the DSC thermogram, and crystalline melting point(T_m) about 50℃ was determined at the peak maximum of the highest temperature transition. The glass transition temperature(T_g) of this EMAA[26] copolymer is in the range of 25~32℃.

Thin films of EMAA[26] copolymer for infrared analysis were cast from 1% THF solution(weight /volume) onto KBr windows. After a majority of the solvent had evaporated, the films were transferred to a vacuum dessicator to completely remove residual solvent and were then stored under vacuum over fresh phosphorus pentoxide(P_2O_5) to minimize moisture adsorption. A 1.0 M diethylzinc ($ZnEt_2$) solution in hexane was purchased from Aldrich Chemical Co. The $ZnEt_2$ solution was diluted further with 2-fold anhydrous hexane in a helium purged dry glovebox. The EMAA[26] copolymer films supported on the KBr windows were then transferred to the glovebox and introduced into the dilute $ZnEt_2$ solution. These films were removed and placed in small vacuum dessiccator over fresh P_2O_5 and evacuated for at least 24 h.

Infrared spectra were recorded on a Digilab FTS-60 FT-IR spectrometer at a resolution of 2 cm^{-1} except otherwise noted. A minimum of 64 scans were signal averaged, and the spectra were stored on a magnetic disk system. Spectra recorded at elevated temperatures were obtained by using a SPECAC high-temperature cell mounted in the spectrometer and a Micristar heat controller.

This device has a reported accuracy of ±0.1℃. The sample was heated at a rate of 5℃/min and was held at the set temperature for 10 min to reach an equilibrium. Films used in this study were sufficiently thin to be within an absorbance range where Beer-Lambert law is obeyed.

RESULTS AND DISCUSSION

Band Assignment and Determination of the Degree of Neutralization. Details of the temperature dependence of the infrared spectra of EMAA copolymers attributed to the methacrylic acid structural unit have been presented in a previous paper,[21] and only a brief summary will be given here. In the pure EMAA[26] copolymer at ambient temperatures, carboxylic acid groups exist predominantly as dimers which have a characteristic infrared carbonyl stretching vibration located at 1700 cm^{-1}. The carbonyl stretching vibration of the monomeric carboxylic acid group, which becomes more apparent with increasing temperature occurs at 1750 cm^{-1}. At temperature above about 140℃, bands attributed to the formation of cyclic and linear anhydrides are observed at 1802/1764 and 1780/1735 cm^{-1}, respectively.[21]

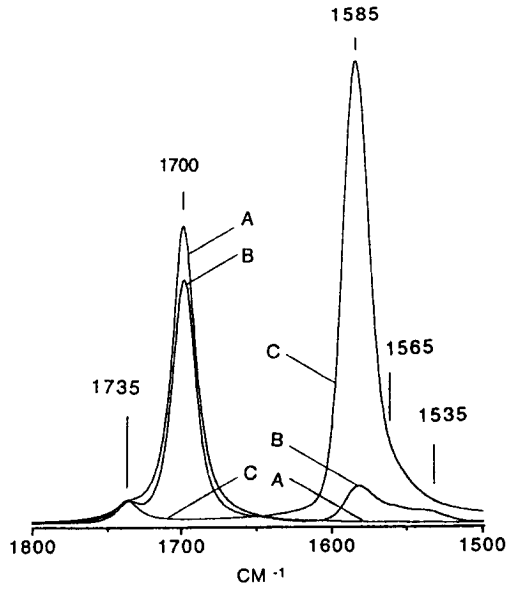


Fig. 1. Scale-expanded infrared spectra recorded at room temperature in the range of 1800~1500 cm^{-1} of EMAA[26] copolymer films with varying degrees of neutralization with zinc ions : (A) pure EMAA[26] ; (B) 20% and (C) 100% neutralized.

Fig. 1 shows both the acid carbonyl and carboxylate stretching regions of room-temperature infrared spectrum of a partially neutralized zinc ionomer. It has been previously shown that the single band at 1585 cm^{-1} associated with the asymmetric carboxylate stretching vibration of the completely neutralized zinc ionomer is consistent with a tetrahedrally coordinated multiplet structure.[11] It can be seen from the coexistence of both carboxylic acid carbonyl stretching vibration at 1700 cm^{-1} and the asymmetric carboxylate stretching vibration at 1585 cm^{-1} in the spectrum of the ionomer film that the partial neutralization has been achieved by the sample preparation method described in the Experimental section. It is also observed that there are two further absorption bands at 1565 cm^{-1}. The pair of weak absorption bands at 1565/1535 cm^{-1} have been assigned to the hexacoordinated zinc carboxylate multiplet.[11,13] In addition, during the synthesis of the EMAA[26] copolymer a minor fraction of the carboxylic acid groups are converted to esters by transesterification and this ester group is characterized by a relatively weak absorbance at 1735 cm^{-1}. This ester impurity at 1735 cm^{-1} does not appear to be affected by both heating and neutralization processes, therefore, it has been used as an internal standard band to estimate the degree of neutralization.[13]

From the spectrum of the pure EMAA[26] film sample, the absorbance ratio of the dimeric carboxylic acid C=O(1700 cm^{-1}) to the ester C=O(1735 cm^{-1}), $A_D°/A_E°$, was obtained. The corresponding absorbance ratio, A_D/A_E, for the partially neutralized zinc ionomer can be measured, and the degree of neutralization is given by

$$\% \text{ neutralization} = \left[1 - \left\{\frac{A_D}{A_E}\frac{A_E°}{A_D°}\right\}\right] \times 100$$

Note that the absorption coefficients for both es-

Table 1. Determination of % Neutralization for EMAA[26]-Zn Ionomer

sample	ester C=O			acid dimer C=O			% neutralization
	frequency cm^{-1}	width cm^{-1}	A_E*	frequency cm^{-1}	width cm^{-1}	A_D*	
pure EMAA[26]	1737	15	0.49	1699	18	9.30	0
partially neutralized	1737	17	3.15	1699	18	47.69	20
fully neutralized	1734	15	0.61	–	–	–	100

* arbitrary units.

ter impurity and carboxylic acid carbonyls cancel out in this equation. The degree of neutralization for the partially neutralized zinc ionomer sample was determined, and the results are summarized in Table 1.

Temperature Studies. Fig. 2 shows the effect of temperature upon both the carboxylic acid carbonyl and carboxylate stretching regions from 1800 to 1500 cm^{-1} of the infrared spectra of the partially neutralized EMAA[26]-Zn ionomer(20% acid groups neutralized). Between room temperature and 100℃ there are no substantial changes observed in the spectra. Above 100℃, however, major spectral changes are observed. First, the bands attributed to hexacoordinated zinc carboxylates(1565 /1535 cm^{-1}) increase in intensity, while the band at 1585 cm^{-1}, associated with tetracoordinated zinc carboxylates, decreases. Second, there is a large decrease in the relative intensity of the carboxylic acid dimer band(1700 cm^{-1}) and a small, but significant, increase in the relative intensity of the monomeric carboxylic acid band at 1750 cm^{-1}, also with increasing temperature. However, there is a temperature limit up to 140℃, because of the onset of anhydride formation. It should also be stated that the identical amount of the synthesized spectrum for the ester impurity was subtracted from each of the experimental spectra because the presence of the ester impurity at 1735 cm^{-1} interferes with the forthcoming quantitative analysis. The most prominent spectral change, however, is the appearance and growth of a new absorption band at 1620 cm^{-1}. This absorption band has been assigned to the zinc acid salt structure,[13,22] which is depicted schematically below.

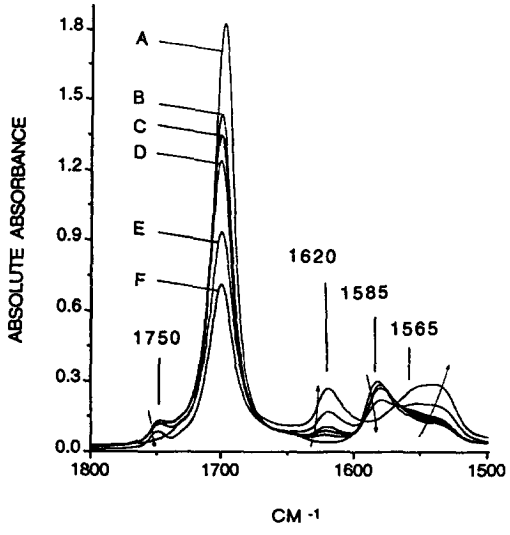
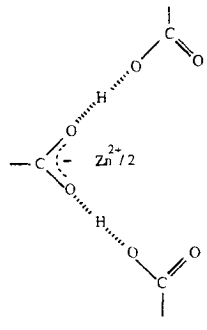


Fig. 2. Infrared spectra in the range of 1800~1500 cm^{-1} of the 20% neutralized EMAA[26]-Zn ionomer recorded as a function of increasing temperature ; (A) room temperature, (B) 100, (C) 110, (D) 120, (E) 130, and (F) 135℃.



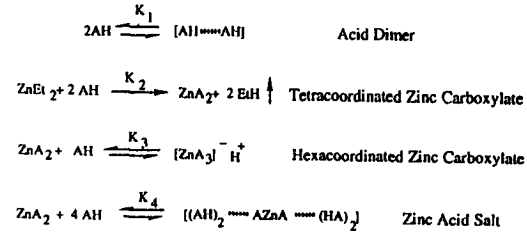
zinc carboxylic acid salt structure

In monomeric carboxylic acid the carbonyl stretching vibration occurs at 1750 cm^{-1}. Assigning the

new absorption band at 1620 cm^{-1} to the carbonyl stretching vibration indicates a surprisingly large frequency shift, 130 cm^{-1}. Since it is unlikely that the carbonyl group of the acid is hydrogen bonded, it has been suggested that when carboxylic acid forms the hydrogen bond, the acid proton moves away from the acid oxygen toward the carboxylate oxygen.[22] As the strength of the hydrogen bond increases the hydrogen atom is not so clearly identified as more strongly associated with the carboxylate oxygen as depicted above. This movement of the acid proton is similar to ionization of the carboxylic acid except that the proton is not removed completely. In this process the carboxylic acid group acquires carboxylate ion character with a result of weakening of the acid carbonyl bond. This causes a very large shift in frequency of about 130 cm^{-1} for the carbonyl band of the carboxylic acid group from 1750 to 1620 cm^{-1}.

Equilibrium Constants and Enthalpies of Hydrogen Bond Formation for Carboxylic Acid Dimerization and Acid Salt Formation. The chemistry occuring in partial neutralization of EMAA copolymer with $ZnEt_2$ has been described by a series of simple equilibria as depicted in Scheme 1.[13]

There are some important implications of the



Scheme 1.

equilibrium scheme presented in Scheme 1. First, in the presence of a stoichiometric equivalent or an excess of zinc cations, the tetracoordinated zinc salt will be formed. It is only when there is a stoichiometric excess of carboxylic acid groups that zinc acid salts and the hexacoordinated zinc salt are formed.

Fig. 3 shows the infrared spectra of the same sample employed in Fig. 2, recorded as a function of decreasing temperature from 135℃ to room temperature. Curve fitting of the carbonyl and carboxylate stretching regions was performed by using a least-squares program on the spectra recorded as the sample was heated to 135℃(Fig. 2) and cooled to room temperature(Fig. 3). Curve-fitting results of the carbonyl stretching region of the temperature-dependent infrared spectra are

Table 2. Curve-Fitting Results of the C=O Stretching Region of the Spectra Recorded as a Function of Temperature for the 20% Neutralized EMAA[26]-Zn Ionomer

Temperature ℃	Carboxylic acid dimer C=O band			Carboxylic acid monomer C=O band				Carboxylic acid-salt C=O band			
	Frequency cm^{-1}	Width cm^{-1}	Area	Frequency cm^{-1}	Width cm^{-1}	Area	Fraction* monomer C=O	Frequency cm^{-1}	Width cm^{-1}	Area	Fraction* acid-salt C=O
25	1699	18	48.49								
100	1701	20	41.94	1745	22	1.93	0.069	1630	30	1.55	0.052
110	1701	20	40.32	1746	21	2.21	0.081	1625	30	2.36	0.079
120	1701	20	37.74	1746	20	2.53	0.097	1621	30	3.58	0.121
135	1700	22	31.39	1748	15	1.89	0.088	1619	27	9.59	0.308
120	1700	22	31.58	1748	17	1.57	0.074	1619	29	9.85	0.316
110	1700	21	32.48	1748	16	1.49	0.068	1619	28	9.93	0.313
100	1700	21	32.97	1748	16	1.25	0.057	1620	25	9.98	0.313
80	1699	20	32.24	1750	16	0.77	0.037	1621	25	10.05	0.325
25	1699	19	35.12					1621	23	10.35	0.320

* absorptivity ratio[21] = 1.6.

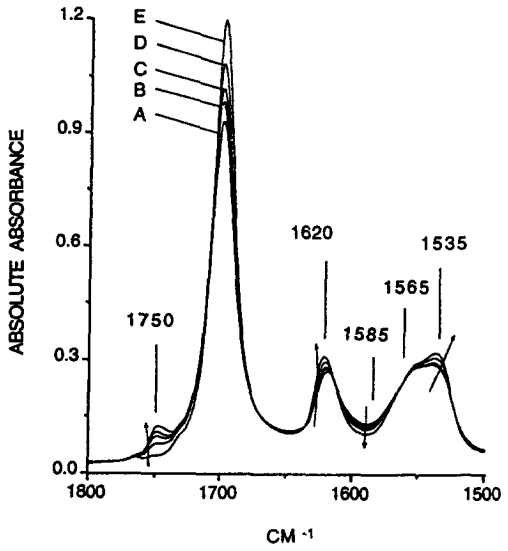


Fig. 3. Infrared spectra in the range of 1800~1500 cm^{-1} of the 20% neutralized EMAA[26]-Zn ionomer recorded as a function of decreasing temperature : (A) 120, (B) 110, (C) 100, (D) 80, and (E) room temperature.

summarized in Table 2. An absorptivity ratio[21] of 1.6 is assumed for the ratio of the carbonyl stretching vibrations of the carboxylic acid dimer to the carboxylic acid monomer(or to the acid salt). Quantitative estimation of the fraction of the monomeric carboxylic acid carbonyls, f_A, and of the acid salt carbonyls, f_{AS}, for the temperature-dependent infrared spectra are also given in Table 2.

Having obtained a quantitative estimation of the fractions of f_A and f_{AS} as a function of temperature, a van't Hoff plot of ln K's versus 1/T can be prepared using the relationships(see Appendix for the derivation) :

$$K_1=\frac{0.8(1-f_A^2)}{2.56\ f_A^2}$$

$$K_4=\frac{8\ f_{AS}(1+f_A)^3}{(1-f_{AS})(1.6f_A)^4}$$

where K_1 and K_4 are both equilibrium constants for the acid dimerization and acid salt formation, respectively. Such plots are shown in Fig. 4 and 5. An estimation of the enthalpies of carboxylic acid

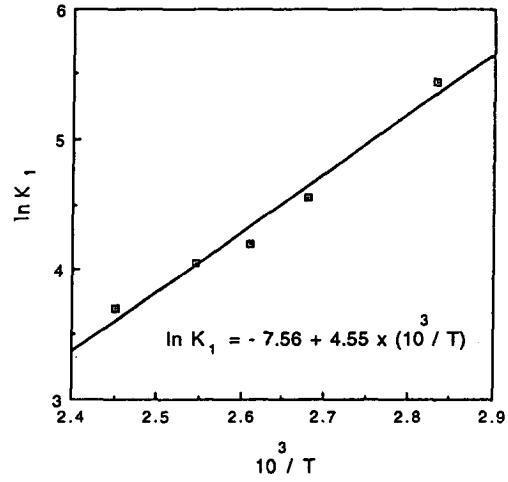


Fig. 4. van't Hoff plot(ln K_4 vs. 1/T) of the equilibrium constant for the carboxylic acid dimerization of the 20% neutralized EMAA[26]-Zn ionomer.

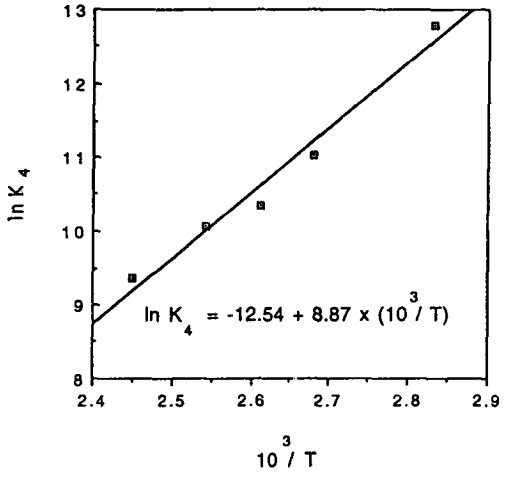


Fig. 5. van't Hoff plot(ln K_4 vs. 1/T) of the equilibrium constant for the carboxylic acid salt formation of the 20% neutralized EMAA[26]-Zn ionomer.

dimerization and acid salt formation were determined from the slope of the van't Hoff plots yielding values of −4.55 and −8.87 kcal/mol, respectively. From these results it may be deduced that the strength of hydrogen bond of the zinc carboxylic acid salt is almost two times greater than that of the carboxylic acid dimer in the partially neutralized zinc ionomer. It has been reported that the enthalpy for the acid dimerization of the pure

EMAA copolymer was −6.95 kcal/mol.[21] The enthalpy of −4.55 kcal/mol for the acid dimerization of the partially neutralized EMAA[26]-Zn ionomer is smaller than that of the pure EMAA copolymer.

SUMMARY

Temperature dependent infrared studies of a partially neutralized EMAA[26]-Zn ionomer were presented. Unionized carboxylic acid groups remaining in the partially neutralized EMAA[26]-Zn ionomer form two types of hydrogen bonds : carboxylic acid dimers and carboxylic acid salts. Thermodynamic parameters of these hydrogen bonds formations were calculated using integrated absorbances giving enthalpies of −4.55 and −8.87 kcal /mol for the acid dimerization and carboxylic acid salt formation in the partially neutralized EMAA [26]-Zn ionomer, respectively. The behavior of carboxylic acid groups in the partially neutralized EMAA[26]-Zn ionomer is not similar to that of the parent carboxylic acid copolymer. It is shown that the carboxylic acid monomer-dimer equilibrium in the partially neutralized EMAA[26]-Zn ionomer is affected by the formation of the carboxylic acid salts.

APPENDIX

Derivation of the Relationship for the Equilibrium Constants K_1 and K_4. The chemical equation of the carboxylic acid dimerization and acid salt formation may be depicted as shown in Scheme 1 :

$$AH + AH \underset{}{\overset{K_1}{\rightleftharpoons}} [AH\cdots AH] \quad \text{acid dimerization}$$

$$ZnA_2 + 4\,AH \underset{}{\overset{K_4}{\rightleftharpoons}} [(AH)_2\cdots AZnA\cdots (HA)_2] \quad \text{zinc acid salt}$$

where AH, [AH···AH], ZnA_2, and [$(AH)_2$··· AZnA···$(HA)_2$] represent the monomeric, dimeric carboxylic acids, tetracoordinated carboxylate, and acid salt, respectively. K_1 and K_4 are the equilibrium constants for carboxylic acid dimerization and acid salt formation, respectively. K_1 and K_4 are defined as

$$K_1 = \frac{\xi_{AA}}{\xi_A \xi_A} \tag{1}$$

$$K_4 = \frac{\xi_{AS}}{\xi_{ZnA_2} \xi_A} \tag{2}$$

where ξ_A, ξ_{AA}, ξ_{ZnA_2}, and ξ_{AS} are the mole fraction of AH, [AH···AH], ZnA_2, and [$(AH)_2$···AZnA··· $(AH)_2$] units, respectively, in the partially neutralized EMAA[26]-Zn ionomer at equilibrium.

$\xi_A + \xi_{AA} + \xi_{ZnA_2} = 1$

$\xi_{ZnA_2} = 0.2$, since the percent neutralization of the ionomer prepared in this study is 20%,

$$\text{thus } \xi_{AA} = 0.8 - \xi_A \tag{3}$$

The fraction of monomeric acid carbonyl groups can be measured at different temperatures and may be given by

$$f_A = \frac{\xi_A}{\xi_A + 2\xi_{AA}} \tag{4}$$

where f_A is the fraction of monomeric carboxylic acid carbonyl groups experimentally measured at equilibrium(Table 2).

Substituting Eq. 3 into Eq. 4

$$f_A = \frac{\xi_A}{1.6 - \xi_A} \tag{5}$$

Rearranging yields :

$$\frac{1}{f_A} = \frac{1.6}{\xi_A} - 1$$

$$\xi_A = \frac{1.6 f_A}{1 + f_A} \tag{6}$$

Substituting Eq. 6 into Eq. 3

$$\xi_{AA} = 0.8 - \frac{1.6 f_A}{1 + f_A} = \frac{0.8(1 - f_A)}{1 + f_A} \tag{7}$$

The substitution of Eqs. 6 and 7 into Eq. 1 leads to

$$K_1 = \frac{\dfrac{0.8(1 - f_A)}{1 + f_A}}{\left(\dfrac{1.6 f_A}{1 + f_A}\right)^2} = \frac{0.8(1 - f_A^2)}{2.56 f_A^2}$$

Substituting $\xi_{ZnA_2}=0.2$ into Eq. 2

$$K_4=\frac{\xi_{AS}}{0.2\xi_A^4} \tag{8}$$

The fraction of acid salt carbonyl groups can be measured at different temperatures and may be given by

$$f_{AS}=\frac{\xi_{AS}}{\xi_{AS}+\xi_A+2\xi_{AA}} \tag{9}$$

where f_{AS} is the fraction of acid salt carbonyl groups experimentally measured at equilibrium (Table 2).

Rearranging yields :

$$\frac{1}{f_{AS}}=1+\frac{f_A}{\xi_{AS}}+\frac{2\xi_{AA}}{\xi_{AS}}$$

$$\xi_{AS}=\frac{f_{AS}(\xi_A+2\xi_{AA})}{1-f_{AS}} \tag{10}$$

Substituting Eqs. 6 and 7 into Eq. 10

$$\xi_{AS}=\frac{\frac{1.6f_{AS}}{1+f_A}}{1-f_{AS}}=\frac{1.6f_{AS}}{(1+f_A)(1-f_{AS})} \tag{11}$$

The substitution of Eqs. 6 and 11 into Eq. 8 leads to

$$K_4=\frac{8f_{AS}(1+f_A)^3}{(1-f_{AS})(1.6f_A)^4}$$

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